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LUMINOPHORES BASED ON STRONTIUM ALUMINATES PRODUCED BY THE SOL-GEL METHOD

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Luminophores based on strontium aluminates activated by europium and dysprosium ions are synthesized using the sol-gel method. The effect of a ratio between strontium and aluminum ions on crystallization and luminescent properties of the luminophores produced is investigated. It is demonstrated that the degree of dispersion of luminophore powders is 3 – 4 μm . In contrast to the traditional solid-sintering method, the stage of milling materials can be eliminated.

Evolution and upgrade of telecommunications and electronics require new types of highly effective luminescent materials. Lately special interest is focused on a group of luminophores based on aluminates of alkali-earth metals (AEM) activated by rare-earth ions, for instance $\text{SrAl}_{12}\text{O}_{19}:\text{Ce}$; $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}$, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$. Such crystal-phosphors are used in projection screens, field emission and plasma displays, scanning systems, etc. [1 – 4].

A distinctive feature of luminophores based on AEM monoaluminates activated simultaneously by two rare-earth element (REE) coactivators is possibility of obtaining long-term phosphorescence (U.S. Patents Nos. 5424006 and 6117362) [5, 6]. These crystal-phosphors are capable of effectively accumulating light energy and then emitting it in darkness for a long time, up to several days. Compared to classical zinc sulfide luminophores, they have several valuable properties: high radiation intensity, color purity, longer afterglow, and good chemical, thermal, and radiation resistance. Such luminophores can find wide application as light sources, passive indication systems, in road safety devices, as a basis for luminescent paints and fillers for films, in polygraphy (luminescent inks), in diverse signal systems and electronic control panels.

To increase the efficiency of light-emitting materials, new principles and methods of synthesis are used, in particular, the sol-gel method. The Department of Chemical Engineering of Glass and Glass Ceramics at the D. I. Mendeleev Russian Chemical Engineering University has been conducting research of the physicochemical principles of the sol-gel method for production of luminescent materials based on high-melting oxides: zinc, yttrium and alkali-earth element silicates and strontium aluminates [7 – 9].

The purpose of our study was to use the sol-gel method for synthesis of luminophores in the $\text{SrO} - \text{Al}_2\text{O}_3$ system activated by europium and dysprosium ions and to study the effect of the ratio $\text{SrO}:\text{Al}_2\text{O}_3$ on the phase composition and luminescent properties of materials. This line of research is interesting for two reasons. On the one hand, it is known that various crystalline luminescent phases are formed in this system: SrAl_2O_4 , SrAl_4O_7 , and SrAl_2O_6 [10, 11]. On the other hand, in production of luminophores by the sol-gel method, variations in the ratio $\text{Sr}:\text{Al}_2\text{O}_3$ have an effect on the gel structure, since the precursor is aluminum isobutylate, which in hydrolysis and polycondensation forms a gel. The content (here and elsewhere molar content, unless otherwise specified) of the main oxides varied within the following limits (%): 40.8 – 65.7 strontium, 33.0 – 58.0 aluminum, which corresponded to the ratio $\text{SrO}:\text{Al}_2\text{O}_3 = 0.7 - 2.0$. The ratio $\text{EuO}:\text{SrO}$ was kept constant: 0.02 mole/mole, whereas the content of Dy^{3+} ions varied within the limits of 0.1 – 0.5%.

The initial components for preparing homogenous solutions were aluminum isobutylate $\text{Al}(\text{OC}_4\text{H}_9)_3$, crystalline strontium nitrate, REE oxides, bidistilled water, ethyl alcohol, and nitric acid. Gel formation was performed at a temperature of 60°C, and drying of gel at 100 – 500°C. Gels were heat-treated in a temperature interval of 700 – 1300°C for 1 h in a reducing atmosphere, which is needed for the transition of europium ions into the bivalent state.

The behavior of gels under heating in a temperature interval of 20 – 1000°C was studied on a Q-1500 derivatograph (Paulik – Paulik – Erday). Crystallization properties were investigated on a DRON-3 plant (CuK_α radiation) in an interval of $2\theta = 10 - 60^\circ$ with sensitivity of $(1 - 2) \times 10^3$ pulses/sec. Radiation spectra were registered using a spectrophotometric set with the following main modules: a DB-15-1 lamp with a UGS-1 light filter, a UM-2 monochro-

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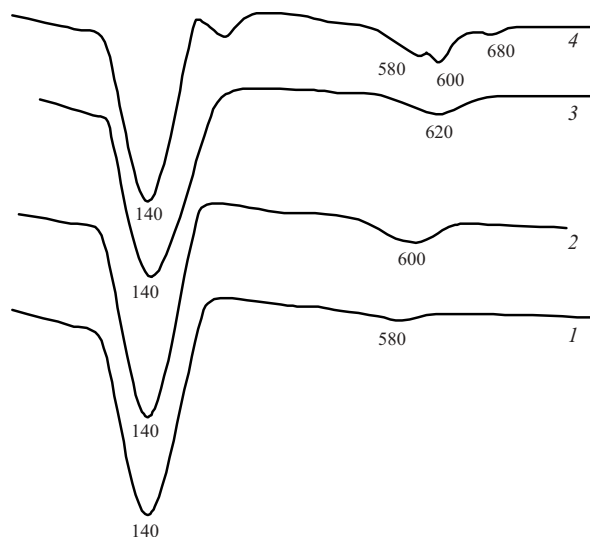


Fig. 1. Thermograms of samples with ratio $\text{SrO} : \text{Al}_2\text{O}_3$ equal to 0.70 (1), 0.98 (2), 1.47 (3), and 2.00 (4).

mator, a FEU-51 photoelectron multiplier, and a M-95 brightness meter. Afterglow characteristics were measured at the laboratory of luminescence of Platan Scientific and Research Association. The dispersion of the samples synthesized was estimated by the photosedimentation method.

Regardless of a content of aluminum isobutylate, the gel formation process started already in mixing of the initial solution and ended within 1 h with formation of homogenous semi-opaque gels. The structure of moist gel largely determines the structure of the target material and its properties. To study the processes occurring in heating gels of different chemical compositions, differential thermal analysis was carried out (Fig. 1). All thermograms exhibit endothermic effects at 140°C and in a temperature interval of 560–680°C. The presence of a low-temperature endothermic effect is related to the removal of water, excessive solvent, and product of hydrolysis from gel. The position of this endothermic effect does not depend on the ratio of reactants in the initial solution. In contrast, the type and the shape of the endothermic effects at temperatures of 560–680°C are determined by decomposition and removal of nitric oxides and significantly vary depending on the gel composition. Thus, in gel with a

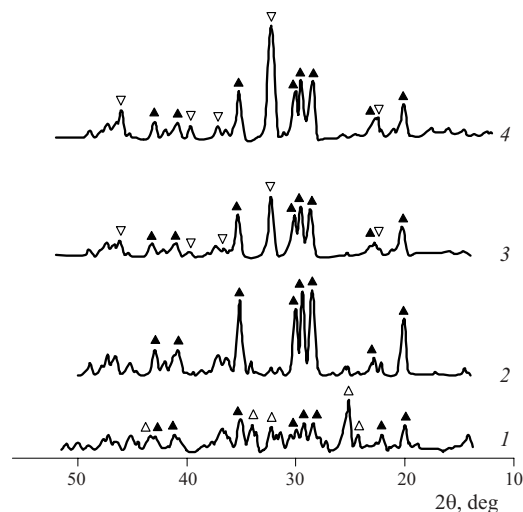


Fig. 2. Diffraction patterns of samples with ratio $\text{SrO} : \text{Al}_2\text{O}_3$ equal to 0.70 (1), 0.98 (2), 1.47 (3), and 2.00 (4) after thermal treatment for 1 h at 1300°C: \blacktriangle SrAl_2O_4 ; ∇ SrAl_4O_7 ; \triangle $\text{Sr}_3\text{Al}_2\text{O}_6$.

minimum quantity of strontium oxide (Fig. 1, curve 1), a slight endothermic effect is registered at 580°C. As the content of strontium oxides grow to 67.5% (curve 4), the endothermic effect is shifted toward higher temperatures (600–680°C) and becomes more complex and intense.

The results of x-ray phase analysis of gels heat-treated at 1300°C demonstrated that several crystalline phases are formed depending on the ratio of the main components (Fig. 2). With the ratio $\text{SrO} : \text{Al}_2\text{O}_3$ greater than 1, strontium monoaluminate SrAl_2O_4 and three-strontium aluminate $\text{Sr}_3\text{Al}_2\text{O}_6$ crystallize, with the ratio $\text{SrO} : \text{Al}_2\text{O}_3$ less than 1, strontium mono- and dialuminate SrAl_4O_7 are formed. In a sample containing 49% SrO and 50% Al_2O_3 , only strontium monoaluminate SrAl_2O_4 crystallizes. Thus, the course of the crystallization process depends on the particular field of phase crystallization in the phase diagram, in which the particular composition falls.

Luminophores after thermal treatment mainly had a green glow, the color and brightness of luminescence significantly depending on the phase composition of materials. Figure 3 shows photoluminescence spectra of materials synthesized. It can be seen that the maximum luminescence brightness is seen in samples with the ratio $\text{SrO} : \text{Al}_2\text{O}_3$ within an interval of 0.98–1.47. Table 1 shows the phase composition of the samples and luminescent properties of the materials obtained. It is known [5, 6] that in contrast to ions Eu^{3+} , which yield red radiation in any matrix, the position of the radiation spectrum for Eu^{2+} ions depends on the matrix, into which these ions are introduced. Analyzing the data on photoluminescence, one can infer that Eu^{2+} ions incorporated into the strontium monoaluminate structure instead of ions Sr^{2+} and form solid solutions ensuring green luminescence with the maximum wavelength of 520 nm [5,6]. In compositions with the ratio $\text{SrO} : \text{Al}_2\text{O}_3$ higher than 1, which simulta-

TABLE 1

Ratio $\text{SrO} : \text{Al}_2\text{O}_3$	Phase composition	Maximum wavelength, nm	Photo- emission brightness, arb. units	Color coordinates	
				x	y
2.00	$\text{Sr}_3\text{Al}_2\text{O}_6$, SrAl_2O_4	520	110	0.269	0.570
1.47	$\text{Sr}_3\text{Al}_2\text{O}_6$, SrAl_2O_4	520	250	0.262	0.563
0.98	SrAl_2O_4	520	180	0.255	0.555
0.70	SrAl_2O_4 , SrAl_4O_7	490	20	0.159	0.382

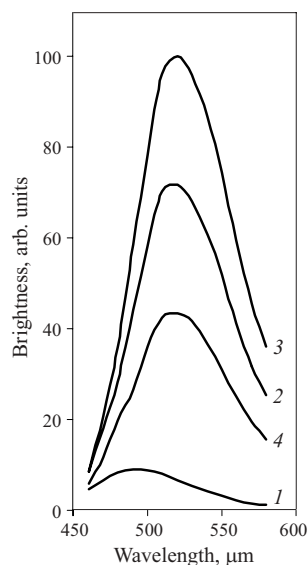


Fig. 3. Photoluminescence spectra of luminophores with ratio $\text{SrO}:\text{Al}_2\text{O}_3$ equal to 0.70 (1), 0.98 (2), 1.47 (3), and 2.00 (4) excited by UV radiation (wavelength 264 nm).

neously contain mono- and three-strontium aluminates, Eu^{2+} ions as well radiate in the green spectrum range.

At the same time, the radiation maximum of Eu^{2+} ions in samples containing 40.8% CaO and crystallizing with formation of strontium dialuminates shifted to a shorter wavelength range, from 520 to 490 nm, which is accompanied by a perceptible modification of brightness and color coordinates of luminescence of luminophores.

Introduction of dysprosium oxide into the luminophore composition does not change the type of luminescence: the emission spectrum maximum is at 520 nm, however, Dy_2O_3 even in small quantities (0.1%) causes a perceptible increase in the brightness and duration of afterglow. The mechanism of phosphorescence of strontium aluminates depends on recombination processes and a variation of the degree of oxidation of activator ions Eu^{2+} and Dy^{3+} [6]. As a consequence of processing data on the curves of afterglow brightness decrease of luminophores produced by the sol-gel method with different contents of Dy_2O_3 , it was found that the duration of scintillation of accumulated light to a brightness level of 0.3 mcd/m^3 reaches tens of hours.

An important service parameter for light-emitting materials, apart from luminescent properties, is the granulometric composition of powders. According to the existent technology, luminophores based on aluminates are synthesized by solid-phase sintering of aluminum oxide and carbonates of AEM (U.S. Patent No. 5424006) [6] at temperatures above $1300 - 1500^\circ\text{C}$. As a consequence, materials with large sizes of luminophore grains are formed: $100 - 200 \mu\text{m}$. Since the fraction normally used is $15 - 30 \mu\text{m}$, the next stage of synthesis consists of milling and fractionation to a preset degree of dispersion. A distinctive characteristic of materials based on strontium aluminates is the fact that when the powders are milled to a preset granulometric composition, the brightness of luminescence abruptly decreases: two- or threefold.

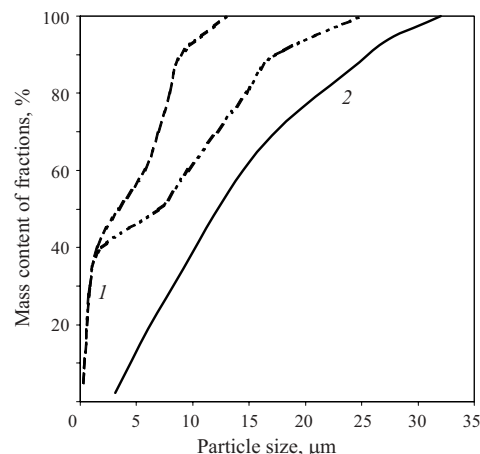


Fig. 4. Integral curves of size distribution of particles for sol-gel sample (1) and sample synthesized by traditional method (2).

One of the obvious advantages of the sol-gel method is the possibility of obtaining finely dispersed materials, up to nanopowders [12, 13]. To estimate the grain size of sol-gel luminophores, the granulometric composition of powders was analyzed and compared with parameters of materials synthesized according to the traditional technology. Figure 4 shows integral curves of size distribution of particles. In using the traditional method, the mean size of the grains was $17 \mu\text{m}$, and specific surface area was $0.3 \text{ m}^2/\text{g}$. In powders produced by the sol-gel technology, the average size of grains was $3.5 \mu\text{m}$ without additional milling and the specific surface area was $13 \text{ m}^2/\text{g}$. Processes of agglomeration of particles intensify in fine-dispersion powders with an extended specific surface area. The majority of grains of the sol-gel luminophore apparently exists in the agglomerated state. An evidence of this is the inflection in the curve of size distribution of particles. The average size of grains of sol-gel luminophores is presumably $1 - 2 \mu\text{m}$, and large particles constitute agglomerates of finer particles.

The obtained data clearly demonstrate that application of sol-gel technology allows for a substantial decrease in the size of luminophore grains and makes it possible to exclude such energy- and labor-consuming operations as powder milling and screening, in which luminescence parameters of materials significantly deteriorate.

Thus, the sol-gel method can become the most suitable for synthesis of phosphorescent materials based on strontium aluminates.

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